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(54) Title: LUBRICANT COMPOSITION CONTAINING MIXED FRICTION MODIFIERS

(57) Abstract

The present invention provides an improved lubricating oil composition for automotive internal combustion engines and transmission which comprises an oil of lubricating viscosity having admixed therewith a minor amount of friction modifier composition which reduces the coefficient of friction between moving mechanical parts, thereby providing for enhanced fuel economy. The friction modifier composition comprises a combination of an alkoxylated hydrocarbyl amine and a polyol partial ester of a saturated or unsaturated fatty acid or mixture of such esters, each preferably present in the range of from about 0.1 to about 1.0 % by weight based on the weight of the oil. This combination of components provides for synergistic fuel economy effects particularly when used as components in automotive crankcase lubricants also containing conventional additive packages, which effects are not observed in oil which contains one or the other of these components alone.

dispersancy, viscosity stability, corrosion, oxidation inhibition and the like.

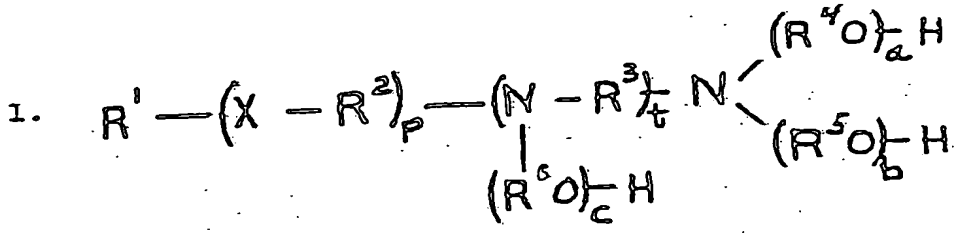
Representative examples of known oil additive modifiers are found in U.S. Patent No. 3,933,659 which discloses fatty acid esters and amides; U.S. Patent No. 4,176,074 which describes molybdenum complexes of polyisobutenyl succinic anhydride-amino alkanols; U.S. Patent 4,105,571 which discloses glycerol esters of dimerized fatty acids; U.S. Patent No. 3,779,928 which discloses alkane phosphonic acid salts; U.S. Patent No. 3,778,375 which discloses reaction products of a phosphonate and oleamide; U.S. Patent No. 3,852,215 which discloses S-carboxy-alkylene hydrocarbyl succinimide, S-carboxyalkylene hydrocarbyl succinic acid and mixtures thereof; U.S. Patent 3,879,306 which discloses N-(hydroxy-alkyl) alkenyl-succinamic acids or succinimides; U.S. Patent No. 3,932,290 which discloses reaction products of di-(lower alkyl) phosphites and epoxides; and U.S. Patent No. 4,028,258 which discloses the alkylene oxide adduct of phosphosulfurized N-(hydroxyalkyl) alkenyl succinimides.

Another known category of friction modifiers includes alkoxylated hydrocarbyl mono or polyamines such as generally illustrated by formulas 1 and 2 below. These amines include materials such as N,N-bis(2-hydroxyalkyl) hydrocarbyl amines such as disclosed in U.S. Patents 3,711,406, 3,796,662, 3,933,659, 4,010,106, 4,129,508, 4,170,560, 4,231,883 and 4,795,583.

providing for enhanced fuel ecomony. The friction modifier composition comprises a combination of an alkoxylated hydrocarbyl amine and a polyol partial ester of a saturated or unsaturated fatty acid or a mixture of such esters. This combination of components provides for synergistic fuel ecomony effects, particularly when used as components in automotive crankcase lubricants also containing conventional additive packages, which effects are not observed in oil which contains one or the other of these components alone.

DETAILED DESCRIPTION

The alkoxylated amines which are suitable as one component of the friction modifier composition of this invention have the general formula 1:

1. 

and also include boronated derivatives thereof, wherein R^1 is a branched or straight chain hydrocarbyl group containing from about 8 to about 30 carbon atoms, R^2 and R^3 are independently the same or different branched or straight chain alkylene radicals containing 1 to 6 carbon atoms, R^4, R^5 and R^6 are independently the same or

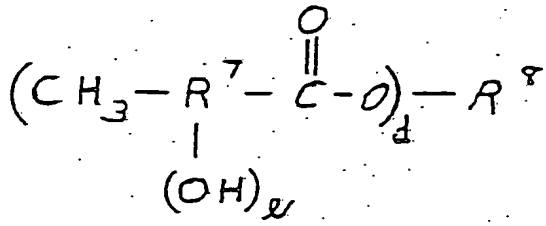
derived from tallow amine, oleyl amine, stearyl amine, lauryl amine, behynyl amine and the like as well as mixtures thereof, R^4 and R^5 each contain 2 or 3 carbon atoms, and a = b = 1.

Illustrative of more preferred alkoxylated amines within the scope of this invention include N,N',N'-tri(2-hydroxyethyl) N-octadecyl propylene diamine, N,N',N'-tri(2-hydroxyethyl) N-octadecenyl propylene diamine, N,N',N'-tri(2-hydroxyethyl) N-hexadecyl propylene diamine, N,N',N'-tri(3-hydroxypropyl) N-octadecadienyl propylene diamine, N,N',N'-tri(2-hydroxyethyl) N-octadecyl ethylene diamine, N,N',N'-tri(2-hydroxyethyl) N-octadecenyl ethylene diamine, N,N',N'-tri(2-hydroxyethyl) N-tetradecyl propylene diamine, N,N-di(2-hydroxyethyl) oleyl amine, N,N-di-(2-hydroxyethyl) stearyl amine, N,N-di(3-hydroxypropyl) tetradecyl amine, N,N-di(2-hydroxyethyl) octadecylamine, N,N-di(2-hydroxyethyl) eicosylamine, N,N-di(2-hydroxyethyl) tallowamine, N,N-di(2-hydroxypropyl) tallowamine, N-(2-hydroxyethyl)-N-(hydroxyethoxyethyl)-n-dodecylamine,
N,N-di(2-hydroxyethyl)-1-methyl-undecylamine,
N,N-di(2-hydroxyethoxyethoxyethyl)-1- ethyl-octadecylamine,
N,N-di(2-hydroxyethyl)-n-dodecyloxyethylamine,
N,N-di(2-hydroxyethyl)-lauryloxyethylamine,
N,N-di(2-hydroxyethyl)-stearyloxyethylamine,
N,N-di(2-hydroxyethyl)-n-dodecyloxpropylamine,
N,N-di(2-hydroxyethyl)-stearyloxypropylamine,
N,N-di(2-hydroxyethyl)-dodecylthioethylamine,
N,N-di(2-hydroxyethyl)-dodecylthiopropylamine,
N,N-di(2-hydroxyethyl)-hexadecylthioethylamine,
N,N-di(2-hydroxyethyl)-hexadecylthiopropylamine,

can be used and is often desirable for certain applications. Thus, boronation can be complete or partial. Usually boronation levels vary from about 0.05 to about 7 weight % of boron in the boronated derivative.

Preferably the boronated derivatives are prepared in the presence of an alcoholic or hydrocarbon solvent. The presence of a solvent is not essential, however. If one is used, it may be reactive or non-reactive. Suitable non-reactive solvents include benzene, toluene, xylene and the like. Suitable reactive solvents include isopropanol, butanol, the pentanols and the like. Reaction temperatures may vary from about 70° to about 250°C with about 110° to about 170°C being preferred.

The second essential component of the friction modifier composition of this invention is one or a mixture of esters of a fatty acid having the formula 3:

3. 

wherein R^7 represents an alkylene or alkenylene hydrocarbyl radical having from 10 to 18 carbon atoms, R^8 is the residuum of a polyhydric alcohol containing from 2 to 5 carbon atoms and from 2 to 4

paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils.

Synthetic lubricating oils include hydrocarbon and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes); alkylbenezenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl) benzenes); and polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenols).

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification or etherification constitute another class of known synthetic lubricating oils. These are exemplified by polyoxylalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, and include the alkyl and aryl ethers of these polyoxyalkylene polymers such as methyl-polyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of poly-ethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500, and mono-and polycarboxylic esters thereof such as acetic acid esters, mixed C_3 to C_6 fatty acid esters and the C_{13} Oxo acid diester of tetraethylene glycol.

poly(methyl)siloxanes and poly(methylphenyl) siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

Unrefined, refined and rerefined oils can be used in the lubricants of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art. Rerefined oils are obtained by processes similar to those used to obtain refined oils, but applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

The components of the friction modifier composition of this invention are each blended into the lube oil base stock in amounts which reduce the friction

complete disclosure of which is incorporated herein by reference. Such dispersants are generally added to the oil in amounts ranging from about 0.1 to about 10% by weight.

Metal containing rust inhibitors and/or detergents are frequently used with ashless dispersants. Such detergents and rust inhibitors include the metal salts of sulphonic acids, fatty acid esters such as glycerol mono and/or di stearate (which also function as friction modifiers), alkyl phenols, sulfurized alkyl phenols, alkyl salicylates, naphthenates, and other oil soluble mono- and di-carboxylic acids. Highly basic, that is overbased metal salts, which are frequently used as detergents include calcium or magnesium phenates, sulfurized phenates and/or sulfonates. Usually these metal containing inhibitors and detergents are used in lubricating oil in amounts of about 0.01 to 10 wt. %, more preferably about 0.1 to 5 wt. %, based on the weight of the total lubricating composition. Marine diesel lubricating oils typically employ such metal-containing rust inhibitors and detergents in amounts up to about 20 wt. %.

The lube oil may also contain one or more suitable antioxidants and/or oxidation inhibitors. Suitable antioxidants include phenols, hindered phenols, bis-phenols, sulfurized phenols, catechol, alkylated and sulfurized alkylated catechols, diphenylamine, alkylated diphenylamines and phenyl-1-naphthlamines, alkyl and aryl borates, phosphites and phosphates, trialkyl and triaryl dithiophosphates and the like. Other antioxidants

The copper antioxidants will generally be added to the oil in an amount of from about 50-500 ppm by weight of the metal.

Corrosion inhibitors, also known as anti-corrosive agents, reduce the degradation of the metallic parts contacted by the lubricating oil composition. Illustrative of corrosion inhibitors are phosphosulfurized hydrocarbons and the products obtained by reaction of a phosphosulfurized hydrocarbon with an alkaline earth metal oxide or hydroxide, preferably in the presence of an alkylated phenol or of an alkylphenol thioester, and also preferably in the presence of carbon dioxide. Phosphosulfurized hydrocarbons are prepared by reacting a suitable hydrocarbon such as a terpene, a heavy petroleum fraction of a C_2 to C_6 olefin polymer such as polyisobutylene, with from 5 to 30 weight percent of a sulfide of phosphorus for 0.5 to 15 hours, at a temperature in the range of 150° to 600°C. Neutralization of the phosphosulfurized hydrocarbon may be effected in the manner taught in U.S. Patent 1,969,324.

Oxidation inhibitors reduce the tendency of mineral oils to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and viscosity growth. Such oxidation inhibitors include alkaline earth metal salts of alkylphenolthioesters having preferably C_5 to C_{12} alkyl side chains, calcium nonylphenol sulfide, barium t-octylphenyl sulfide, dioctylphenylamine, phenylalphanaphthylamine, phosphosulfurized or sulfurized hydrocarbons, etc.

Illustrative alkyl groups include isopropyl, isobutyl, n-butyl, sec-butyl, amyl, n-hexyl, methylisobutyl carbinyl, heptyl, 2-ethylhexyl, diisobutyl, isooctyl, nonyl, behenyl, decyl, dodecyl, tridecyl, etc. Illustrative lower alkylphenyl groups include xylyl, cresyl, butylphenyl, amylphenyl, heptyl-phenyl, etc. Cycloalkyl groups likewise are useful and these include chiefly cyclohexyl and the lower alkyl-cyclohexyl radicals. Many substituted hydrocarbon groups may also be used, e.g., chloropentyl, dichlorophenyl, and dichlorodecyl.

These compounds are prepared by first forming the relevant phosphorodithioic acid and then reacting this product with a suitable metal containing compound.

The phosphorodithioic acids are prepared by the reaction of phosphorus pentasulfide with an alcohol or phenol or mixtures of alcohols, mixtures of phenols or mixtures of alcohols and phenols. The reaction involves four moles of the alcohol or phenol per mole of phosphorus pentasulfide, and may be carried out within the temperature range from about 50°C to about 200°C, preferably from about 50°C to about 150°C. Thus the preparation of O,O-di-n-hexyl phosphorodithioic acid involves the reaction of phosphorus pentasulfide with four moles of n-hexyl alcohol at about 100°C for about two hours. Hydrogen sulfide is liberated and the residue is the defined acid. The preparation of the metal salt of this acid may be effected by reaction with metal oxide. Simply mixing and heating these two reactants is sufficient to cause

In one preferred embodiment, the alkyl groups R^9 and R^{10} in the formula above are derived from secondary alcohols such as isopropyl alcohol, secondary butyl alcohol, 2-pentanol, 4-methyl-2-pentanol, 2-hexanol, 3-hexanol, as well as mixtures thereof.

These compounds are generally incorporated into the lubricating oil formulation in the range of from about 0.01 to about 5% by weight, more preferably from about 0.1 to about 3% by weight. The preferred compounds are the zinc dihydrocarbyl dithiophosphites.

Viscosity modifiers impart high and low temperature operability to the lubricating oil and permit it to remain relatively viscous at elevated temperatures and also exhibit acceptable viscosity or fluidity at low temperatures. Viscosity modifiers are generally high molecular weight polymers, including polyesters, polymethacrylates, polyacrylates and polyolefins. The viscosity modifiers may also be derivatized to include other properties or functions, such as the addition of dispersancy properties. These oil soluble viscosity modifying polymers will generally have number average molecular weights of from 10^3 to 10^6, preferably 10^4 to 10^6, e.g., 20,000 to 250,000, as determined by gel permeation chromotography or osmometry.

Examples of suitable hydrocarbon polymers include homopolymers and copolymers of two or more C_2 to C_{30} olefin monomers, e.g. C_2 to C_8 olefins, including both alpha olefins and internal olefins, which may be straight or branched, aliphatic,

Compositions which contain one or more of these numerous additives are typically blended by physical admixture into the lube oil in amounts effective to provide their normal attendant function.

The improved lubrication enhancement offered by compositions within the scope of this invention can be demonstrated using what is referred to as a Sequence VI Dynanometer Fuel Economy test, more specifically described as the ASTM Sequence VI test method RR: D0-2: 1204. This test is run using a 3.8 liter Buick V-6 engine equipped with cooling means to maintain a relatively constant engine oil temperature of 150°F or 275°F, coupled to a power absorbing dynanometer such that the engine speed and power output can be tightly controlled.

The lubricant to be evaluated is first flushed into the engine and aged at an oil temperature of 225 deg. F for 32 hours. The engine is then set to a specific speed and power output, and the test is conducted at the temperature for the two test stages of 150 deg. F and 275 deg. F. The engine is calibrated prior to each candidate run, using industry standard viscosity and friction modified reference oils. At each stage the average brake specific consumption is calculated. After the completion of the measurement stages, the lubricant in the engine is detergent flushed then flushed to an SAE 30 baseline oil and the measurements are repeated. These measurements are then used to calculate the Equivalent Fuel Economy Improvement (EFEI) of the candidate relative to the baseline oil.

Example 1: Control formulation + 0.5% V. glycerol oleate esters

Example 2: Control formulation + 0.5% V. N,N-bis (2-hydroxyethyl) tallow amine

Example 3: Control formulation + 0.25% V. glycerol oleate esters + 0.25% V. N,N-bis (2-hydroxyethyl) tallow amine.

The Control formulation and each of the formulations of Examples 1-3 were subjected to a Sequence VI dynanometer fuel economy screener test. The recorded EFEI test results are as follows:

EFEI Test Result

Control	1.17
Example 1	2.44
Example 2	3.10
Example 3	3.14

The test results show that each of the glycerol oleate mixtures and N,N-bis (2-hydroxyethyl) tallow amine exhibit enhanced fuel efficiency in the base formulation when added to the control formulation at a 0.5% by volume concentration, with the N,N-bis (2-hydroxyethyl) tallow amine being somewhat superior.

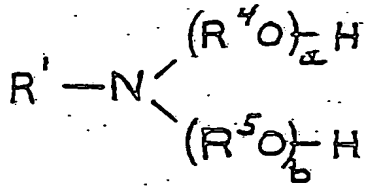
The EFEI result of 3.14 achieved by combining N,N-bis (2-hydroxyethyl) tallow amine and the

Example 4	1.94
Example 5	2.48
Example 6	2.67

These results once again demonstrate the EFEI test results based the combination of N,N-bis (2-hydroxyethyl) tallow amine and the glycerol oleate mixtures each present at a 0.25% by volume concentration are superior to results achieved using N,N-bis (2-hydroxyethyl) tallow amine alone at 0.25% by volume and 0.5% by volume concentrations respectively.

wherein R^7 represents an alkylene or alkenylene hydrocarbyl radical having from 10 to 18 carbon atoms, R^8 is the residuum of a polyhydric alcohol containing from 2 to 5 carbon atoms and from 2 to 4 hydroxyl groups, e is 0 or 1 and d is an integer of 1, 2 or 3.

2. The composition of claim 1 wherein said amine has the formula:



3. The composition of claim 1 wherein R^1 contains from 12 to 24 carbon atoms.

4. The composition of claim 3 wherein R^1 is tallow group.

5. The composition of claim 1 wherein each of R^4, R^5 and R^6 contain 2 carbon atoms.

6. The composition of claim 2 wherein said amine is N,N-bis(2-hydroxyethyl) tallowamine.

7. The composition of claim 2 wherein R^8 is the residuum of glycerol.

8. The composition of claim 7 wherein R^7 contains 14 to 16 carbon atoms.

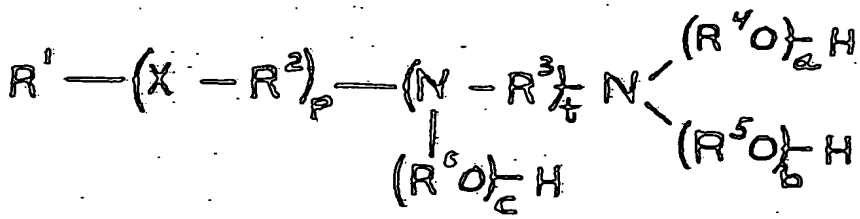
9. The composition of claim 8 wherein (e) is 0.

18. The composition of claim 15 wherein said additive includes a magnesium or calcium sulfonate detergent.

19. The composition of claim 15 wherein said additive includes the reaction product of a polyolefin-substituted succinic anhydride and an alkylene polyamine, or a boronated derivative thereof, as a dispersant.

20. A process for enhancing the friction properties of lubricating oil compositions comprising admixing therewith:

i) from about 0.01 to about 1.0% by weight of an alkoxylated amine having the formula:



wherein R^1 is a branched or straight chain hydrocarbyl group containing from about 8 to about 30 carbon atoms, R^2 and R^3 are independently the same or different branched or straight chain alkylene radicals containing 1 to 6 carbon atoms, R^4, R^5 and R^6 are independently the same or different alkylene radicals containing from 2 to 4 carbon atoms, X is oxygen or sulfur, p is 0 or an integer ranging from 1 to 20, t is independently 0 or 1, and a, b and c are independently integers ranging from 1 to 4; and

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 93/03381

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C10M141/06; C10M163/00; C10M167/00; //(C10M141/06, 129:76,133:08)(C10M163/00,129:76,133:08,133:52,135:10,

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C10M

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	US,A,4 010 107 (K. ROTHERT) 1 March 1977 see column 5, line 4 - line 12 see column 5, line 25 - line 35 ---	1,2, 13-21
X	US,A,3 933 659 (R.E. LYLE) 20 January 1976 cited in the application see column 6, line 57 - column 7, line 21 see column 7, line 47 - line 48 see column 8, line 1 see column 8, line 64 - column 9, line 39 see column 15, line 39 - line 40 --- -/--	1-3,5, 7-9,13, 14,15, 16,19, 20,21

° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
21 JULY 1993	02. 08. 93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	HILGENGA K.J.

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9303381
SA 73030

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 21/07/93
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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EP-A-0314843	10-05-89	None		
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